Hydrodechlorination of Perchloroethylene with Swellable Organically-Modified Silica (SOMS)

A Bachelor's of Science Thesis

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Abstract

Groundwater is an important resource to residential, industrial, and agricultural sectors. Unfortunately, chlorinated compounds such as perchloroethylene and trichloroethylene can contaminate groundwater sources due to heavy industrial use. Current methods of groundwater treatment are costly and slow. In this paper, it is suggested that hydrodechlorination be used as a means to remove chlorinated compounds from groundwater. Current hydrodechlorination efforts, however, are hindered by the deactivating effects of ionic species inherent in groundwater on metal catalysts usually used for hydrodechlorination. It is suggested that if a different support were used for the catalyst rather than the traditional Al_2O_3 support, the catalyst could be better protected. The suggested material is Swellable Organically-Modified Silica (SOMS). It is expected that the swellable nature of SOMS will increase the number of available sites and the hydrophobic quality of SOMS will help to repel groundwater ionic species. Therefore, in this paper, the hydrodechlorination activity, quantified by percentage of conversion of perchloroethylene, was compared between both fresh and poisoned commercial (1%Pd/Al_2O_3) and synthesized (1%Pd/SOMS) catalysts. It was determined that when poisoning effects are not considered, the commercial catalyst achieves better conversion, with 95% conversion of perchloroethylene in four hours. When the poisoning effects of NaCl and NaHS are considered, however, the drop in hydrodechlorination activity is significantly more for the commercial catalyst versus the synthesized catalyst. These findings suggest that the SOMS support better protects the Pd when in the presence of poisoning ionic species. IR transmission spectra were also collected for the poisoned catalysts, in order to better understand the effect of the poisons on the surface functional groups. It was determined that sulfur containing species greatly impact the functional group, while the SOMS material better repels the water in the poisoning solutions.

Dedication

Dedicated to my parents and the family I have built at Ohio State

Acknowledgements

I would first like to thank Dr. Umit S. Ozkan, who has been my Principle Investigator and allowed me to be an undergraduate research assistant of the Heterogeneous Catalysis Research Group (HCRG) for the last two years. Her support as I pursued my interest in research, both at Ohio State and in other institutions during the summer months, has been invaluable. Being a member of HCRG has significantly improved my understanding of chemical engineering, specifically related to catalysis and kinetics, and has provided me the confidence and skillset necessary to pursue research at the graduate level. I am so grateful for her guidance and support as I completed this honors research distinction thesis- without her assistance and encouragement, it could not have been completed.

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Nomenclature

General

FTIR Fourier Transform Infrared Spectroscopy

HPLC High Pressure Liquid Chromatography

IR Infrared Region Spectroscopy

ppm Parts Per Million

Chemicals

AC Activated Carbon

Al_2O_3 Aluminum Oxide

Au Gold

C Carbon

Cl^- Chlorine Ion

CCl_4 Carbon Tetrachloride

CNF Carbon Nanofibre

C_2H_4 Ethene

Fe Iron

HCl Hydrochloric Acid

HSAG High Surface Area Graphite

HS^- Hydrogen Sulfide Ion

H_2 Hydrogen

H_2O Water

KBr Potassium Bromide

NaCl Sodium Chloride

NaHS Soidum Hydrosulfide

Na_2SO_4 Sodium Sulfate

NaOH Sodium Hydroxide

NPs Nanoparticles

O_2 Oxygen

PCE Perchloroethylene

Pd Palladium

PdO Palladium Oxide

SOMS Swellable Organically-Modified Silica

SO_4^{2-} Sulfate Ion

TCE Trichloroethylene

THF Tetrahydrofuran

Calculations

A_i Area of retention peak for component i

$C_{i,0}$ Initial concentration of species i

C_i Concentration of species i

n_i moles of species i

V_{loop} Volume of HPLC sample loop

X_i Conversion of species i

$\boldsymbol{\beta_i}$ Calibration factor for species i

$\boldsymbol{\lambda}$ Fraction of hydrogen in volume of HPLC sample loop

1. Introduction

Chlorinated compounds such as perchloroethylene (PCE) have been used heavily in industry for decades, as they are useful solvents that can degrease fats, oils, waxes, and resins [2]. PCE specifically is used as a dry cleaning agent and metal degreaser [3]. A figure of the molecular compound of PCE is included below as Figure 1. In 1980, the US produced 347,000 metric tons of PCE alone [2], and while this number had dropped to approximately 207,700 metric tons by 2011 [3], the amount of PCE being produced annually is still significant. According to the U.S. Department of Health and Human Services, PCE can enter the environment in one of three ways- air, water, or soil. PCE that is released into the air most often stems from dry-cleaning operations and takes a significant amount of time to break down, meaning that it can be transported large distances. Both metal degreasing and dry cleaning industries release liquid wastes that consist partially of PCE, which can end up in groundwater sources. Lastly, soil can become contaminated with PCE if it is near a waste disposal site that is not properly closed off. PCE is slow to break down in water and soil as well, and it has the potential to travel upwards from these mediums into the air of homes and buildings [3].

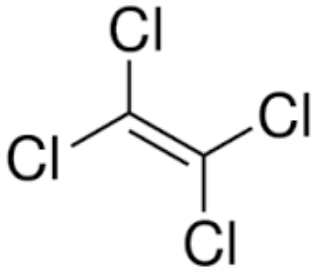

Figure 1: Molecular compound PCE[4]

When PCE is present in water, it can enter one's body and access the stomach, lungs, and eventually the bloodstream when one drinks the water or is in contact with the water. When PCE

is present in the air, which after occurs after PCE evaporates from water sources, it can enter one's body and enter the bloodstream and other organs when breathed in [3]. While PCE is not especially detrimental to the environment, it can severely impact human health if exposure levels are high enough. PCE has been proven to cause kidney and liver damage along with cancer in animals, and is considered a carcinogen to humans and especially harmful to the reproductive system [3,5].

Groundwater sources are a significant resource for agricultural, industrial, and residential use throughout the world. In the United States alone, 77,500 million gallons of groundwater are used daily [1]. As groundwater is a substantial pathway for PCE to affect human health as well as a major source of water for society, it must be carefully monitored and treated in order to ensure that it is not carrying PCE.

Current methods of reducing PCE along with other chlorinated compounds from waterways include air stripping, biotreatments, adsorption, and chemical treatments. In air stripping, the low Henry's Law constant and water solubility of chlorinated compounds is taken advantage of, as air is flowed constantly over the subsurface in order to pull PCE from the water [6]. Disadvantages of this method include that as PCE concentration decreases, the volume of air required quickly becomes physically infeasible, and the end result is that PCE is still present, simply in another medium. This type of process is called a recovery based remediation technique. This means that the PCE still needs to be treated, which makes air stripping and other recovery based remediation techniques costly. A promising alternative to air stripping in order to achieve PCE reduction is biotreatment, in which microorganisms produce enzymes and cofactors that convert chlorinated compounds to carbon dioxide, water, and chlorine [6]. While this is an attractive technology, it is not entirely developed and is currently a slow and

incomplete process. Another recovery based technique is adsorption, which uses activated carbon to adsorb the chlorinated compounds. The advantage of this method is that it can be used for a large variety of toxins and emissions, but a disadvantage is that the adsorbents require regeneration, which causes the process to be inefficient and expensive [7]. An additional procedure to reduce PCE in groundwater is the use of chemical treatments, such as oxidation. In this method, the chlorinated compounds are destroyed through combustion; however, more toxic compounds have the potential to form [6]. Based on the various inefficiencies and disadvantages of each of the aforementioned techniques, a reaction entitled hydrodechlorination is being suggested as a promising alternative.

Hydrodechlorination is the reaction of a chlorinated compound with hydrogen on a catalyst to produce hydrocarbons and hydrochloric acid [8]. A reaction sequence of hydrodechlorination is included below as Equation 1.1.

$$PCE + 5H_2 \rightarrow C_2H_6 + 4HCl \qquad \text{(Eq. 1.1)}$$

Benefits of hydrodechlorination reactions over other more traditional reduction methods include that it produces few toxic byproducts and is a quick and efficient method, as catalysts can be used in situ [9]. While multiple catalysts have been used in hydrodechlorination projects, the metal Palladium (Pd) catalyst has been most effective in carbon-chloride bond cleavage, so that was the only metal tested in this project. Use of Pd is especially promising because it can affect a wide array of contaminants [9]. The traditional catalytic support used for hydrodechlorination is aluminum oxide (Al_2O_3). This current method of hydrodechlorination, however, can be severely affected by ionic species inherent in the groundwater that effectively deactivate the remediation catalysts. The ions that will be addressed in this project will be the sulfate (SO_4^{2-}) ion, the hydrogen sulfide (HS^-) ion, and the chlorine (Cl^-) ion. Several studies

indicate that high concentrations of and long exposure to sulfur ions can lead to catalytic deactivation, and it is expected that hydrogen sulfide ions specifically adsorb to active catalyst sites irreversibly to produce sulfur-containing species that are no longer available for hydrodechlorination [10]. It is suggested that chlorine ions deactivate catalysts through the reduction of the amount of available active sites for chlorinated compounds such as PCE [11]. Another factor that can lead to decreased efficiency of hydrodechlorination is the ever increasing presence of HCl (a product of hydrodechlorination). The increased levels of HCl cause an increased level of acidity around the catalyst which can promote the accumulation of carbonaceous materials, which reduces the catalytic activity [12]. The current deactivation issues plaguing hydrodechlorination hinder its ability to be a feasible means of treating groundwater. In this research project, it is suggested that if a support other than Al_2O_3 were used that could better protect the Pd catalyst, hydrodechlorination could prove more effective.

The suggested support is Swellable Organically-Modified Silica (SOMS), a figure of the chemical compound used to synthesize SOMS is included below as Figure 2. This material is highly absorptive, hydrophobic, and swellable upon contact with organics [13, 14, 15, 16]. It was anticipated that if the Pd catalyst were placed within the swollen matrix of SOMS, then it could be better protected from deactivating ionic species. It was also hypothesized that the hydrophobicity of the SOMS material could repel the groundwater, and hence the ionic species in it. Absorption was also considered to be an advantage, as it was expected that the high absorption rate of SOMS would lead to more available sites, which could help increase hydrodechlorination activity. If this hypothesis proved to be correct, the field of hydrodechlorination as well as groundwater remediation would be significantly advanced.

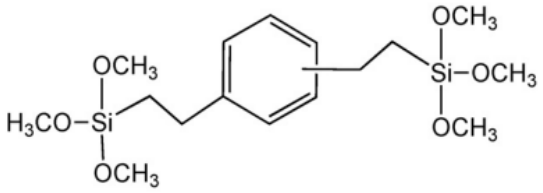

Figure 2: Molecular compound of SOMS [17]

In the present work, the poisoning effects of three types of ions (hydrogen sulfide, sulfate, and chlorine) on hydrodechlorination with both the Pd/Al_2O_3 catalyst and Pd/SOMS catalyst were examined. The Pd/Al_2O_3 catalyst was commercially available, while the Pd/SOMS catalyst was synthesized in lab. The hydrodechlorination reactions were carried out in an aqueous phase batch reactor, and the product stream was analyzed with High Pressure Liquid Chromatography (HPLC) in order to determine PCE conversion. Characterization studies were also conducted to determine the textural properties of SOMS through the use of IR. The results of the hydrodechlorination and characterization studies will be included in this report.

2. Literature Review

In this section of the thesis, a literature review will be conducted that indicates the previous research that has been done in the field of hydrodechlorination. The references that will be discussed will be grouped by topic. Each reference listed has proven useful to the current research project.

2.1 Various Catalytic Supports Tested for Hydrodechlorination

In "Degrading perchloroethene at ambient conditions using Pd and Pd-on-Au reduction catalysts," the catalytic properties and activities of Palladium nanoparticles (Pd NPs), Palladium-on-gold nanoparticles (Pd-on-Au NPs), and Pd/Al_2O_3 were tested and compared [18]. The hydrodechlorination of PCE was performed at room temperature and ambient pressure, and was testing whether the nanoparticles demonstrated "volcano-shape" activity dependence of PCE hydrodechlorination. The results indicated that for the Pd-on-Au NPs, the highest PCE conversion was achieved when percent surface coverage of Pd to Au was 80%- higher percent coverage yielded lower activity. They also indicated that the 80% Pd-on-Au NPs achieved higher rates of conversion than the Pd NPs or the Pd/Al_2O_3 catalyst. This research is important to the current research project, as it demonstrates the importance of surface coverage when comparing various catalytic supports and further elucidates the importance of hydrodechlorination as a groundwater remediation technique.

The research conducted in "Performance of carbon nanofibres, high surface area graphites, and activated carbons as supports of Pd-based hydrodechlorination catalysts" analyzes the hydrodechlorination activity achieved by Pd catalysts on three different carbonaceous supports [19]. The paper indicates that the high surface area graphite (HSAG) supported catalyst achieves best PCE conversion (over Pd/activated carbon and Pd/carbon nanofibre), as the Pd/AC

catalyst is deactivated by coke formation, and the Pd/CNF catalyst is deactivated by coke formation, active phase sintering, and chlorine poisoning. This paper highlights the importance of research into catalytic supports that promote high surface area, such as SOMS.

The paper "Carbon nanofibre-supported palladium catalysts as model hydrodechlorination catalysts" investigates the hydrodechlorination activity achieved by several different palladium catalysts [20]. The properties of different catalysts were adjusted through changing the metal loading, nature of solvent, and support. The results of the experiments indicate that the use of an aqueous solvent increases catalytic activity, but also increases the rate of catalytic deactivation. The chemistry of the support also affected the availability of active sites which markedly impacted the performance of the catalysts. This paper is important to the current work because it highlights the significant effect the catalytic support can have on hydrodechlorination activity and emphasizes the need for more research in the area of catalytic supports.

In "Nanoscale Pd/Fe bimetallic particles: Catalytic effects of palladium on hydrodechlorination" various amounts of Pd loaded on Fe are tested for hydrodechlorination activity. It was determined that the optimal content of Pd for Pd/Fe particles was 1-5wt% [21]. This paper is important to the current research project as it explores a catalytic support option other than the traditional alumina support, and optimizes the Pd content. In order for the SOMS supported catalyst to be commercially viable, parameters such as Pd content will need to be optimized.

2.2 Effect of Organic Solvents on Hydrodechlorination

In "Catalytic hydrodechlorination of chlorinated ethylenes in organic solvents at room temperature and atmospheric pressure," hydrodechorination of chlorinated ethylenes such as PCE and TCE were tested with various organic solvents on the Pd/C catalyst [22]. Based on the results of this project, methanol is considered the best organic solvent to achieve PCE conversion, and PCE conversion slows significantly in the presence of other chlorinated compounds such as TCE. This research paper is important as it indicates that another parameter that can be altered to increase optimization is the organic solvent being used. It also indicates that the reduction of PCE conversion over time is in part due the competition of TCE and other byproducts that form during hydrodechlorination.

The research paper "Enhancement of the catalytic hydrodechlorination of tetrachloroethylene in methanol at mild conditions by water addition," continues to explore the use of methanol as an organic solvent for the hydrodechlorination reaction of PCE [23]. The results of the paper indicate that when water content of the solution is increased from 0 to 50%, PCE conversion is increased significantly. It is suggested that this is due to the lack of formation of TCE that was observed when 50% or more water was used. This paper is important, as it lends more evidence to the notion that hydrodechlorination selectivity greatly impacts a catalyst's ability to convert PCE.

In the paper "Kinetics of deactivation of Pd/C catalyst repeatedly used in the liquid-phase hydrodechlorination of PCE" the kinetics of the deactivation of the Pd/C catalyst is investigated, when hydrodechlorination is performed in methanol or a 50:50 water:methanol mixture [24]. It was determined that the kinetics of this reaction was first order, and indicated that reused catalysts experienced hydrodechlorination at faster rates than fresh catalysts. This study is

significant to the current project because it reinforces the notion that methanol is an effective solvent for the process to occur in, and also indicates that another important aspect of the SOMS investigation that should be studied is reused catalysts.

2.3 Impactful Parameters on Hydrodechlorination

"Catalytic Hydrodechlorination of Chlorinated Hydrocarbons in a Medium of Sodium Hydroxide Solutions. I: Conversion of Carbon Tetrachloride" is a research paper that investigates the hydrodechlorination of a chlorinated compound over a Pd catalyst on sibunite [25]. It analyzes the effects of several parameters, including initial concentrations of CCl_4 and NaOH, temperature, partial pressure of hydrogen, size of catalyst particles, and Pd content of catalysts. It was determined that reaction rate is governed by the concentration of reactants dissolved in the aqueous phase and the volume of the aqueous phase has no impact on conversion of the chlorinated compound or selectivity. This paper is useful to this current project as it provides more background on the parameters that affect hydrodechlorination.

In "Trichloroethylene Hydrodechlorination in Water Using Formic Acid as Hydrogen Source: Selection of Catalyst and Operation Conditions" formic acid is tested as a hydrogen source for hydrodechlorination, and various supports for Pd are investigated as well (activated carbon, carbon nanofibres, high surface area graphites, alumina, ZSM-5 zeolite) [26]. Several formic acid/TCE ratios were studied, and it was determined that there is an optimum ratio- a higher concentration of formic acid inhibits the reaction. Of the supports studied, it was determined that the carbon nanofibre supported Pd calayst achieves the best conversion. This study is important to the current work because it demonstrates how many parameters can be adjusted to optimize hydrodechlorination activity. Thus it is expected that the fresh SOMS

supported catalyst studied in this research project can be optimized in future work in order to be more commercially viable.

The paper "Efficient Degradation of TCE in Groundwater Using Pd ad Electro-generated H_2 and O_2: A Shift in Pathway from Hydrodechlorination to Oxidation in the Presence of Ferrous Ions" analyzes the impact of the presence of Fe(II) on the degradation of TCE in simulated groundwater [27]. According to the paper, when no Fe(II) is present, hydrodechlorination is the major degradation method that occurs, but when Fe(II) is added, hydrodechlorination effectively stops, and oxidation predominately occurs. This paper demonstrates the severe impact species in groundwater can have on hydrodechlorination and highlights the need for more research on the effect of deactivating species, which is what the current project is investigating.

The abovementioned papers indicate the research that has been conducted in the field of hydrodechlorination. They demonstrate that the Pd catalyst is the most significantly researched metal used as a catalyst, and also indicate that there is substantial interest in finding a catalytic support that results in better conversion of PCE than the traditional Al_2O_3 support. While many catalytic supports were tested in these papers, the SOMS support was not investigated. We believe this novel support is a promising type of support due to its high surface area and hydrophobic and absorptive properties. The research studies presented here also emphasize the importance of the solvent used in hydrodechlorination experiments, as well as other parameters such as Pd loading content and partial pressure of hydrogen. Future work of this particular research project will investigate these parameters.

3. Experimental Methodology

Below the experimental procedure carried out for this research project is described. The main four aspects of the experiment were catalyst preparation, ex-situ poisoning of the catalysts, hydrodechlorination experiments, and characterization studies.

3.1 Catalyst Preparation

In order to compare the effectiveness of the traditional Al_2O_3 support with the suggested SOMS support, each catalyst needed first to be available for hydrodechlorination testing. It was determined that each catalyst-support combination would consist of 1%Pd. The traditional 1%Pd/Al_2O_3 catalyst was commercially available and was thus purchased from Sigma Aldrich. SOMS was obtained from ABS materials. The 1%Pd/SOMS catalyst, however, needed to be synthesized in the lab.

In order to synthesize the 1% Pd/SOMS catalyst, the incipient wetness impregnation (IWI) technique was used, in which 0.0214 g of Palladium Acetate was dissolved in 8 mL of acetone and added to the SOMS dropwise. Addition of Pd solution was continued till SOMS was saturated with Pd solution. Once the saturation was obtained, the SOMS material was dried at room temperature. This addition and evaporation cycle was continued until all Pd solution was consumed. The resulting material was dried at room temperature for 12 hours.

In order to ensure that all Pd was available as a catalytic active site and not bound to oxygen, the palladium on both types of catalysts were reduced. The commercial 1%Pd/Al_2O_3 catalyst was reduced through the application of heat at 350°C for four hours, while the synthesized 1%Pd/SOMS catalyst was reduced through chemical reduction, specifically using $NaBH_4$. This was done because SOMS begins to decompose at 400°C.

Overall, 400 mg of commercial catalyst and 400 mg of synthesized catalyst were needed for this research project. Once both catalyst-support combinations were ready, a portion of each type could be poisoned.

3.2 Ex-situ Poisoning of Catalysts

In this research project, the catalysts were ex-situ poisoned. Ex-situ poisoning refers to the process of introducing a catalyst to a solution of ionic species and stirring, before being filtered and dried. Figure 3 below is a pictorial representation of the overall process. A more detailed discussion of the ex-situ poisoning process will follow the listing of poisoning solutions used.

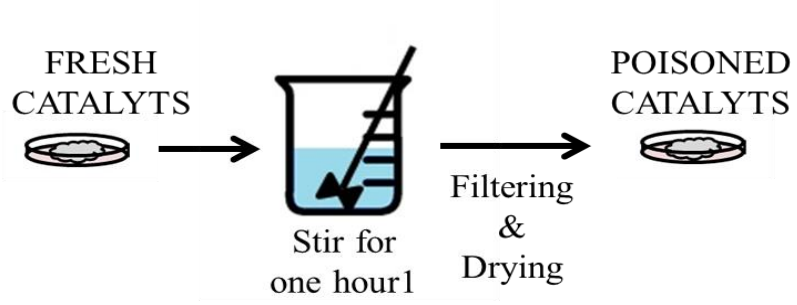

Figure 3: Representation of Ex-Situ poisoning method [17]

The effects of three ionic species were studied in this project: HS^-, SO_4^{2-}, Cl^-. A portion of both the commercial and synthesized catalysts were poisoned by each of these ionic species. Table 1 below indicates the concentrations of each poison and duration of ex-situ poisoning for each groundwater ionic species.

Table 1: Concentration of each type of poison and duration of ex-situ poisoning used on catalysts.

Groundwater Constituents	Concentration	Duration
HS^-	0.1 M	1 hour
SO_4^{2-}	0.1 M	1 hour
Cl^-	0.1 M	1 hour

Each poisoning solution consisted of the ionic species paired with sodium. In order to prepare the different poisoning solutions, a known amount of the poisoning compound was weighed and mixed into a 400 mL of DI water in order to achieve the specified 0.1M concentration. This solution was stirred until a homogeneous mixture was achieved.

Once the poisoning solution was prepared, 0.35 g of catalyst was placed in a three-necked round bottom flask, where it was flushed with Helium. Then 400 mL of the poisoning solution was added to this flask and the resulting solution was stirred for one hour. Flushing with Helium was once again done at the beginning of the poisoning for approximately 5 minutes. After an hour, the solution was filtered using a large Erlenmeyer flask, filter paper, and water pump, and then dried in an oven to evaporate water. Once portions of each type of catalyst were poisoned by each ionic species, they could be used in hydrodechlorination reactions.

3.3 Hydrodechlorination Experiments

In order to assess the abilities of the commercial 1%Pd/Al_2O_3 catalyst and synthesized 1%Pd/SOMS catalyst to reduce PCE, eight hydrodechlorination reactions were carried out in the Heterogeneous Catalysis Research Group's aqueous phase, batch vessel reactor. A picture of this reactor is included below as Figure 4. All hydrodechlorination reactions were carried out at a pressure of 50 bar and a temperature of 30 °C. A 200 mL aqueous solution, which had 1000

ppm of PCE and 450 ppm of tetrahydrofuran (THF) and a volume of ethanol equivalent to the volume of PCE, was first transferred to the reactor. Ethanol was added so that the solubility of PCE could be increased- the solubility of PCE is generally around 120 ppm, but since the initial concentration of PCE is desired to be 1000 ppm, the solubility needed to be increased. After this solution was added to the reactor, 5 mg of catalyst was added to the catalyst addition device, and the reactor was assembled. In order to complete the hydrodechlorination reaction, the reactor was first flushed with an inert gas, which ensured that no air was in the reactor. As the molar amount of hydrogen is more than ten times the molar amount of PCE, the hydrogen is considered to be in excess at all times. After the reactor was flushed, the reactor was heated to 30 °C and pressurized with hydrogen, which ensured that there was a H_2 headspace over the solution. Immediately after the system was pressurized, a sample was taken from the reactor, which was considered the time-zero sample. It was therefore used as the initial concentration of the reaction solution for conversion calculations.

Figure 4: HCRG aqueous phase reactor [17]

The THF solution was used as a means to calculate the final concentration of PCE, as an equation could be obtained that allows one to determine the concentration of PCE as long as one

knows the concentration of another component in the solution. THF is inert in the hydrodechlorination reaction, so if 450 ppm is placed in the reactor, it is known that the final concentration of THF will still be 450 ppm. For this reason, THF is referred to as the internal standard. The process used to calculate the final concentration of PCE will be discussed in further detail in Section 4.1: Concentration and Conversion Calculations.

Every 40 minutes for four hours, a sample was taken with a 1/16" OD sampling tube which could reach the bottom of the reactor. The samples were then analyzed with a High Pressure Liquid Chromatograph (HPLC), which is equipped with a UV/Vis detector (Shimadzu, SPD-20A), and achieves separation with a C18 column. The mobile phase used is a 50:50 solution of acetonitrile and water, and the HPLC is conducted in reverse-phase. During the analysis of samples, the mobile phase undergoes gradient elution to 95:5 acetonitrile and water. The HPLC instrument was used to determine the composition of the stream. The data obtained from the HPLC instrument was reported to a data analysis package which indicated the composition of the product stream through a series of peaks on a retention time plot. The peaks could then be correlated to certain compounds through known retention time data, and the area of the peaks could be correlated to the concentration of each compound in the product stream. This data allowed us to determine the conversion of PCE achieved by each reaction. A depiction of the whole experimental set up is included as Figure 5 below.

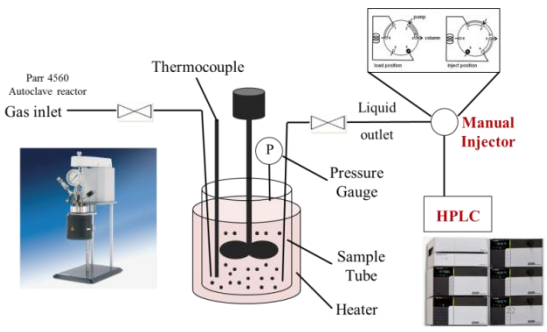

Figure 5: Experimental set-up of hydrodechlorination reactions, including HPLC instrument [17]

The eight hydrodechlorination experiments consisted of four reactions conducted using the commercial 1%Pd/Al_2O_3 catalyst and four reactions conducted using the synthesized 1%Pd/SOMS catalyst. Of these four reactions, one used a fresh catalyst, one used a catalyst poisoned with 0.1M NaHS, another used a catalyst poisoned with 0.1M NaCl, and the last used a catalyst poisoned with 0.1M Na_2SO_4 . The results of these experiments could then be compared to assess catalytic activity. Fresh catalysts with each type of support were used in the experiment to act as a baseline of catalytic activity for the commercial and synthesized catalysts.

3.4 Characterization Studies

In order to better understand the changes of surface functional groups due to poisoning, transmission IR measurements were conducted on the Al_2O_3 and SOMS supported catalysts. A Thermo Nicholet 6700 FTIR equipped with a liquid nitrogen cooled MCT detector was used. Ex-situ poisoned samples were diluted with KBr at a ratio of (1:40). A 0.1 g of sample-KBr physical mixture was transferred to a dye and pressed at 9000 psi for 10 minutes to obtain a disc. Then, the disc was placed in the transmission IR cell holder. To see the effects of poisoning, IR spectra was collected on pristine samples of 1%Pd/Al_2O_3 and 1%Pd/SOMS, and the spectral data of these pristine samples were used as backgrounds. The spectral data was collected at a resolution of 4 cm^{-1} and 512 scans were taken for each catalyst.

4. Results and Discussion

In this section of the report, the results of the hydrodechlorination reactions as well as the characterization studies will be presented and the resulting trends will be analyzed and discussed.

4.1 Concentration and Conversion Calculations

Eight hydrodechlorination experiments were carried out in order to assess the efficacy of the synthesized 1%Pd/SOMS catalyst versus the 1%Pd/ Al_2O_3 catalyst. Samples of each experiment were taken every 40 minutes over a span of four hours and run through an HPLC instrument, which then reported the results to a data analysis package. The data analysis package indicated the composition of the stream through the depiction of peaks on a retention time plot. The area of the peaks allows one to calculate the concentration of each compound in the stream, and hence the conversion of PCE, through the following method.

In order to determine the composition of the product stream reported by the HPLC instrument, calibration of both PCE and THF was needed. A fresh solution, with known concentration of PCE (1000 ppm) and THF (450 ppm), was added to the HPLC six-port valve, which connects to the sample loop. The sample loop has a known volume, V_{loop}, that cannot be exceeded and is much smaller than the syringe volume used to input the solution. Therefore, the same volume of solution enters the HPLC column every test- the remaining solution that was pushed into the HPLC instrument drips out into a waste vial. Since the concentrations of PCE and THF and V_{loop} are known, one can calculate the number of moles of PCE and THF from the following equations, in which n_i refers to the number of moles of species i and C_i refers to the concentration of species i.

$$n_{PCE} = C_{PCE} \times V_{loop} \quad \text{(Eq. 4.1)}$$

$$n_{THF} = C_{THF} \times V_{loop} \quad \text{(Eq. 4.2)}$$

The number of moles of species i can be correlated to the area of the peak on the retention time plot reported by the HPLC data analysis package through calibration factor, β_i, through the following equations, in which A_i refers to the peak area of species i.

$$n_{PCE} = \beta_{PCE} \times A_{PCE} \quad \text{(Eq.4.3)}$$

$$n_{THF} = \beta_{THF} \times A_{THF} \quad \text{(Eq. 4.4)}$$

Therefore, when n_i and A_i is known, the calibration factor for species i can be determined. The calibration factor for THF was determined to be 0.00352 ppm/area, while the calibration factor for PCE was 0.000018 ppm/area. These calibration factors could then be used to determine the number of moles of PCE and THF when the concentrations are not necessarily known, as is the case when taking a sample from the hydrodechlorination reaction.

When considering a solution drawn from the batch reactor, however, one has to consider the fact that there will be a certain fraction of hydrogen along with the expected products, THF, and water. Therefore, when the solution is pushed into the sample loop, a fraction of it will consist of hydrogen. This fraction needs to be taken into account when calculating the number of moles, as simply multiplying the volume of the sample loop by the concentration, if it were known, would overestimate the actual number of moles, because the volume of the sample would be too high. The fraction of the volume that consists of hydrogen needs to be subtracted from the total volume of the sample loop. Therefore, the equations that can be used to calculate the number of moles of PCE and THF in a solution from the batch reaction are included below, where λ refers to the fraction of hydrogen.

$$n_{PCE} = V_{loop}(1 - \lambda) \times C_{PCE} = \beta_{PCE} \times A_{PCE} \quad \text{(Eq. 4.5)}$$

$$n_{THF} = V_{loop}(1-\lambda) \times C_{THF} = \beta_{THF} \times A_{THF} \quad \text{(Eq. 4.6)}$$

By dividing Equation 4.5 by Equation 4.6 and rearranging the result, the concentration of PCE can be calculated. The concentration of THF is known, because it is an inert in the hydrodechlorination reaction. Therefore, if the initial concentration of THF is 450 ppm, then the final concentration is also 450 ppm. For this reason, THF is referred to as the internal standard. Equation 4.7 below demonstrates how to solve for concentration of PCE.

$$C_{PCE} = C_{THF} \times \left(\frac{\beta_{PCE}}{\beta_{THF}}\right) \times \left(\frac{A_{PCE}}{A_{THF}}\right) \quad \text{(Eq. 4.7)}$$

Once the concentration of PCE of a certain sample is determined, the conversion of PCE can be determined for time *t* using Equation 4.8 below, in which X refers to conversion.

$$X_{PCE} = \frac{C_{PCE,0} - C_{PCE,t}}{C_{PCE,0}} \quad \text{(Eq. 4.8)}$$

The raw data for the fresh Pd/Al_2O_3 and Pd/SOMS experiments are included in Appendix A, while sample calculations for concentration and conversion are included in Appendix B. The following section will discuss the results found once conversion of PCE was calculated for all experiments.

4.2 Hydrodechlorination Experiments Results and Discussion

The eight experiments that were conducted compared the conversion achieved by the fresh commercial and synthesized catalysts as well as by the poisoned commercial and synthesized catalysts. A discussion of the concentration and conversion results, organized by poison, is included below.

4.2.1 Fresh Catalytic Activity

The HPLC instrument allowed us to obtain the product distribution of each sample over the span of four hours, through the retention time plots, which can be viewed below. Figures 6 and 7 on the next page are the complete product distribution of the fresh 1%Pd/Al_2O_3 catalyst. Figure 6 indicates that the concentration of PCE drops sharply in the first 80 minutes, with a final PCE concentration of approximately 13 ppm.

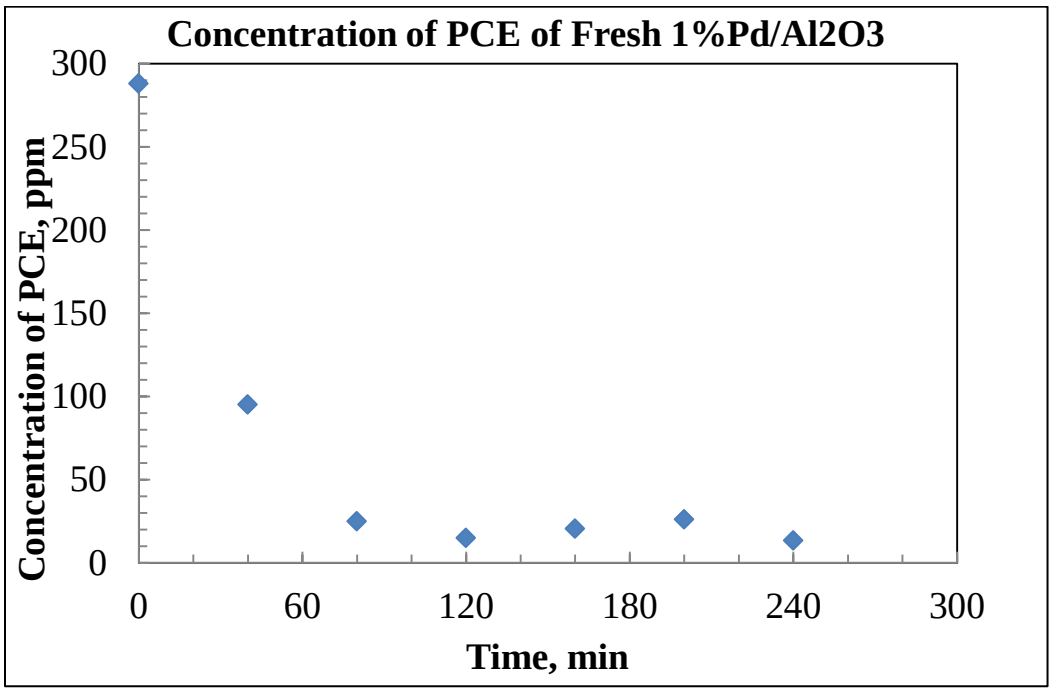

Figure 6: PCE concentration as a function of time for fresh 1%Pd/Al_2O_3 catalyst [28]

Figure 7 on the next page indicates that some side products do form during the hydrodechlorination reaction, but they all similarly have low concentrations of 0 to 1 ppm after four hours.

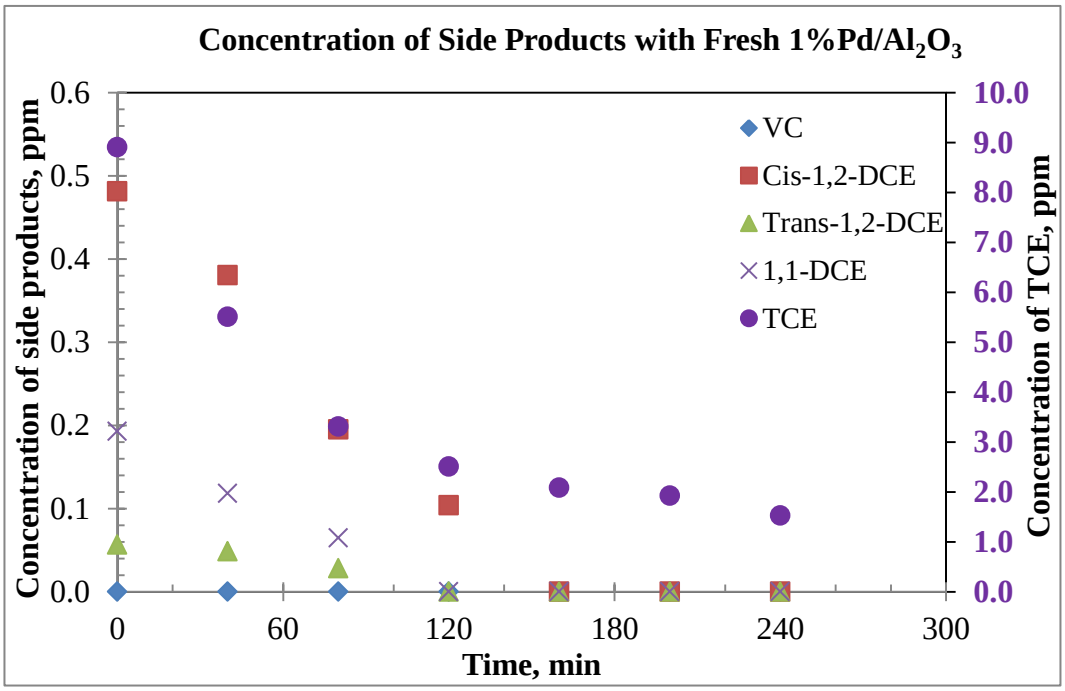

Figure 7: Side product distribution of fresh 1%Pd/Al_2O_3 catalyst [28]

Figures 8 and 9 on the next page are the complete product distribution of the hydrodechlorination reaction achieved with the fresh 1%Pd/SOMS catalyst. When compared to the product concentrations achieved by the fresh 1%Pd/Al2O3 catalyst, it is clear that the SOMS supported catalyst cannot achieve as great a conversion of PCE, and the side products are similarly not converted as effectively. Figure 8 indicates that the final PCE concentration is approximately 33 ppm, while the final concentration of the Al_2O_3 supported fresh catalyst was less than half of that, at 13 ppm. Likewise, the concentration of the side products does not drop appreciably, indicating that the fresh SOMS supported catalyst is not as capable of achieving hydrodechlorination.

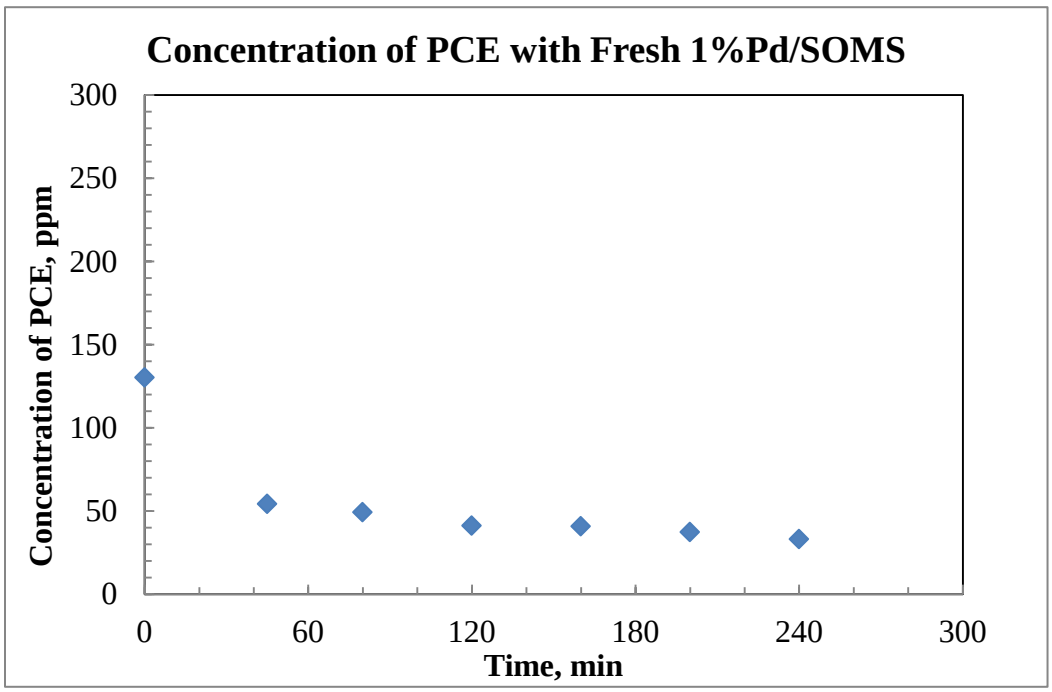

Figure 8: PCE concentration as a function of time for fresh 1%Pd/SOMS catalyst [28]

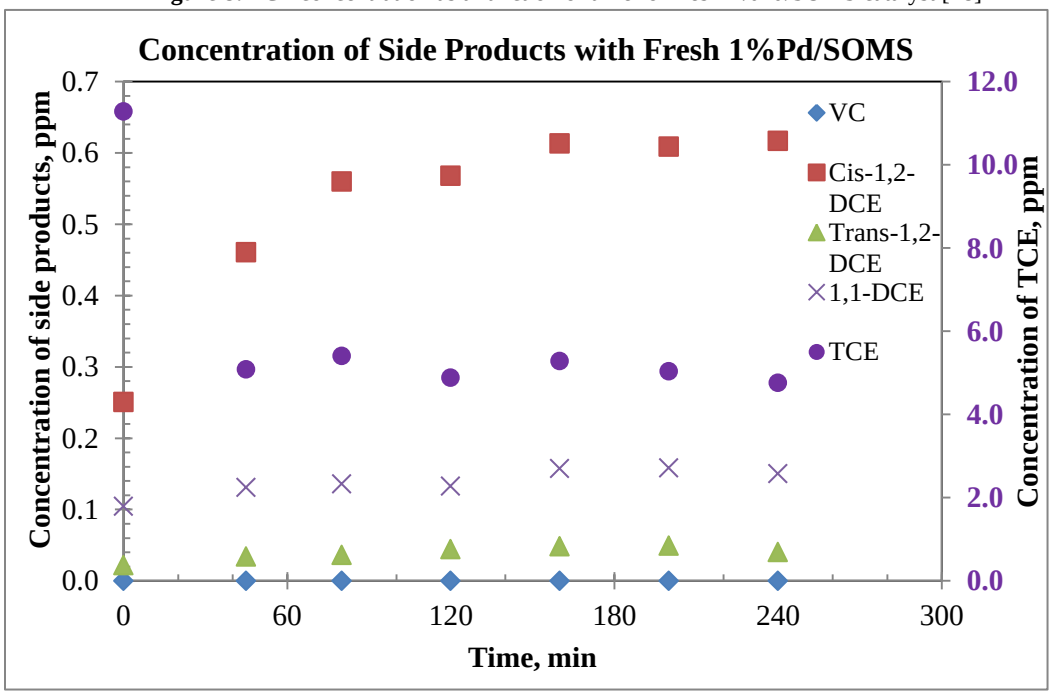

Figure 9: Byproducts concentration as a function of time for fresh 1%Pd/SOMS catalyst [28]

It is important to determine not only the PCE concentrations, but also the PCE conversions achieved by the 1%Pd/ Al_2O_3 catalyst and the 1%Pd/SOMS catalyst without the effect of poisoning. By comparing this baseline activity with the activity of the same, albeit poisoned, catalyst, the impact of the poison on the catalytic performance will be clearly demonstrated. Figure 10 below demonstrates the PCE conversion achieved by both the commercial and synthesized catalysts in four hours.

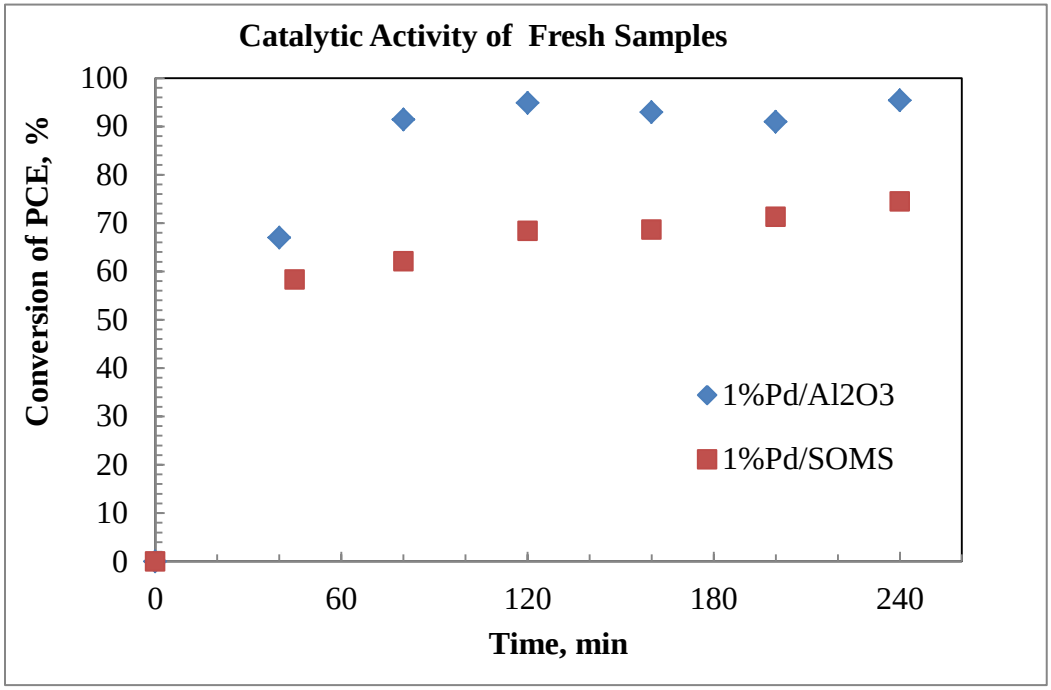

Figure 10: PCE conversion achieved by fresh catalyst [28]

Based on Figure 10 above, when poisoning effects are not considered, the commercial 1%Pd/ Al_2O_3 catalyst performs better than the 1%Pd/SOMS catalyst synthesized in lab. This conclusion can be drawn because the commercial catalyst achieves approximately 95% conversion of PCE in four hours, whereas the synthesized catalyst achieves approximately 75% conversion of PCE in the same time frame, which is a reduction in performance of 20%. The

following sections indicate how the performance of the two types of catalyst-support combinations changes when different poisons are used.

4.2.2 Effect of Poisoning with Na_2SO_4

As discussed previously, both the commercial and synthesized catalysts were ex-situ poisoned with 0.1M Na_2SO_4 for a period of one hour, at which time they were isolated and dried, in order to be used in hydrodechlorination reactions. The performance of the poisoned catalysts could then be compared to the performance of the fresh catalysts. Figures 11 and 12 on the next page indicate the complete product concentration achieved by the 1%Pd/Al_2O_3 poisoned catalyst over a time span of four hours. When comparing these results to the fresh 1%Pd/Al_2O_3 catalyst, one can see that the concentration of PCE drops in a similar manner to the fresh catalyst experiment, resulting in approximately 10.9 ppm of PCE after four hours, which is actually a better rate of conversion than the fresh commercial catalyst. This suggests that the Na_2SO_4 solution does not act as a poison to the Pd catalyst. This conclusion is strengthened when one compares the concentrations of the side products achieved by the hydrodechlorination reaction with the fresh commercial catalyst, as seen in Figure 6, to the Na_2SO_4 poisoned catalyst, as seen in Figure 12. Figures 7 and Figures 12 indicate no significant differences between side product distributions. Based on these results, it can be indicated that the Na_2SO_4 solution does not act as a poison, and does not need to be studied further.

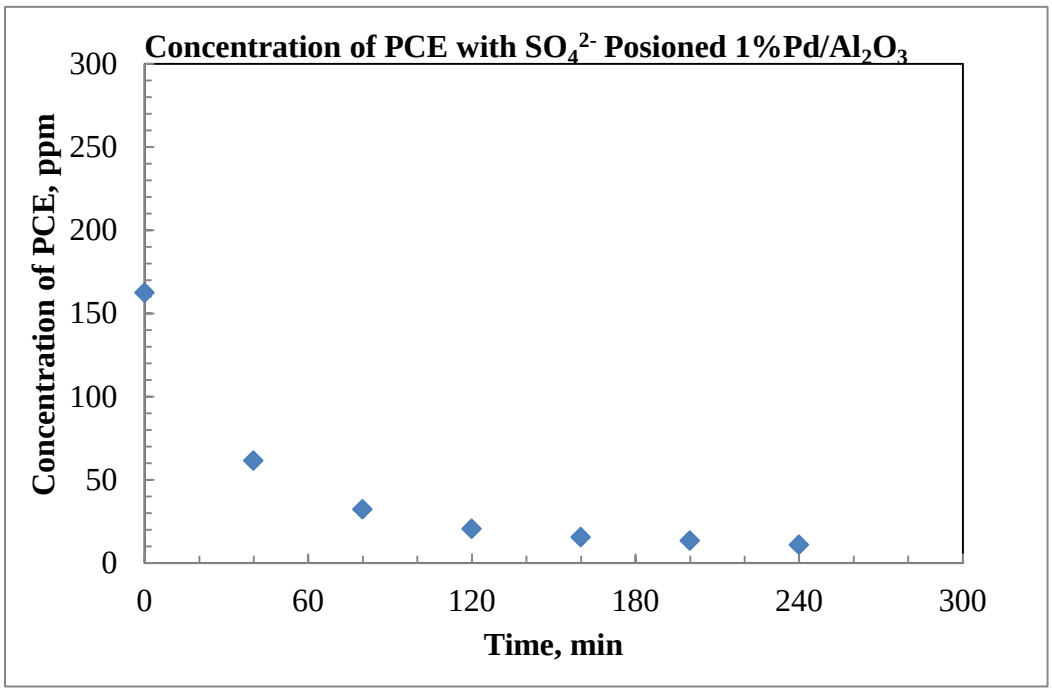

Figure 11: Concentration of PCE as a function of time for Na_2SO_4 poisoned 1%Pd/Al2O3 catalyst [28]

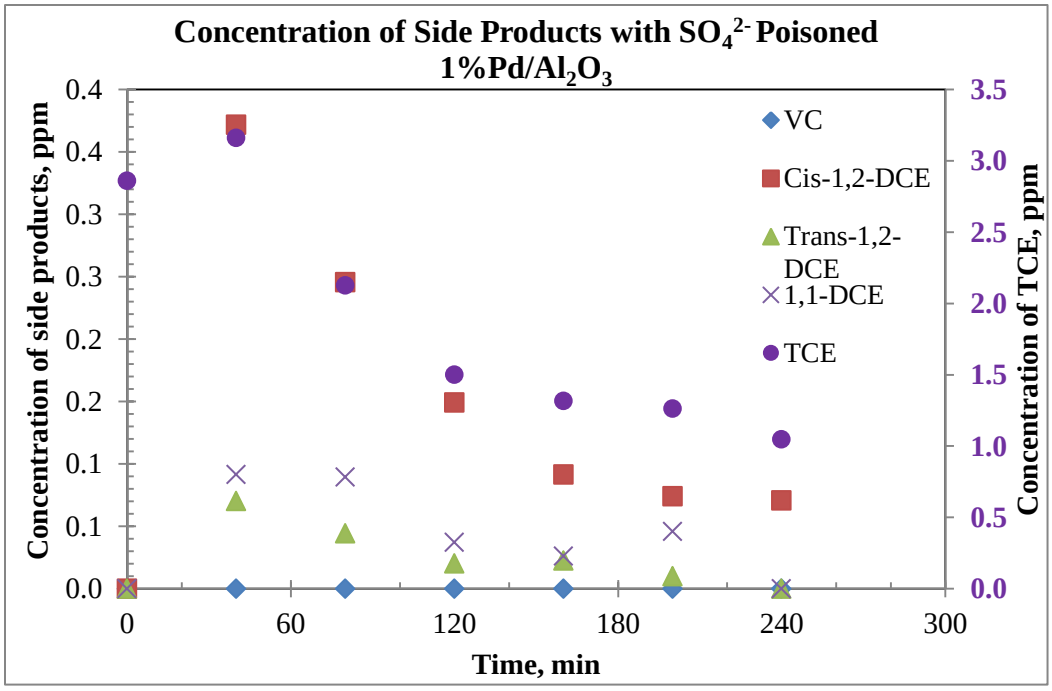

Figure 12: Concentration of side products as a function of time for Na_2SO_4 poisoned 1%Pd/Al2O3 catalyst [28]

The conversion of PCE achieved by the 0.1M Na_2SO_4 poisoned 1%Pd/Al_2O_3 catalyst is included below as Figure 13, along with the conversion of PCE achieved by the fresh commercial catalyst. This graph strengthens the conclusion that the sulfate ion does not act as a poison, as it can be clearly seen that there is no significant difference between PCE conversion of the fresh commercial catalyst and the SO_4^{2-} poisoned Pd/Al_2O_3 catalyst.

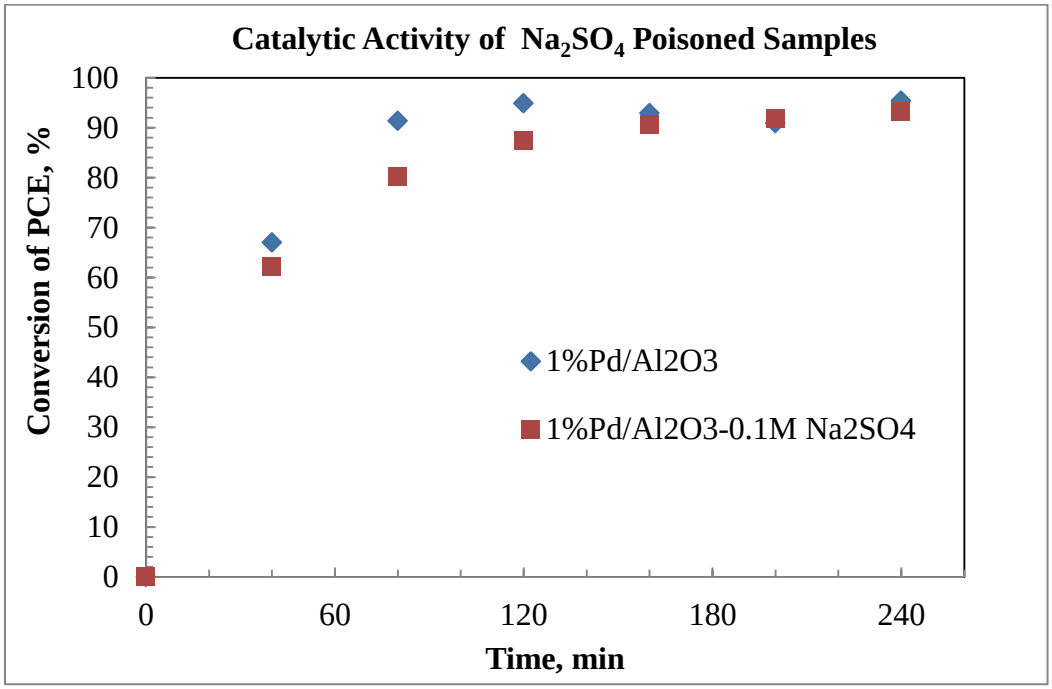

Figure 13: Poisoning effect of Na_2SO_4 on commercial 1%Pd/Al_2O_3 catalyst [28]

4.2.3 Effect of Poisoning with NaCl

Next, the poisoning effect of the Cl^- ion was studied by performing hydrodechlorination experiments with both a NaCl poisoned commercial catalyst and a NaCl poisoned synthesized catalyst. Figure 14 and Figure 15 on the following pages represent the concentrations of PCE and side products achieved after hydrodechlorination by the 0.1M NaCl poisoned 1%Pd/Al_2O_3 catalyst. Comparing the results achieved after four hours with the NaCl poisoned commercial

catalyst to the results achieved with the fresh commercial catalyst, one can see that the concentration of PCE is significantly higher for the NaCl poisoned catalyst, at approximately 43 ppm. Figure 15 indicates a similar trend, as the concentrations of the byproducts of the reaction that used the NaCl poisoned commercial catalyst are significantly higher than those of the reaction that used the fresh commercial catalyst. This suggests that the 0.1M NaCl solution does have a poisoning effect on the Pd catalyst.

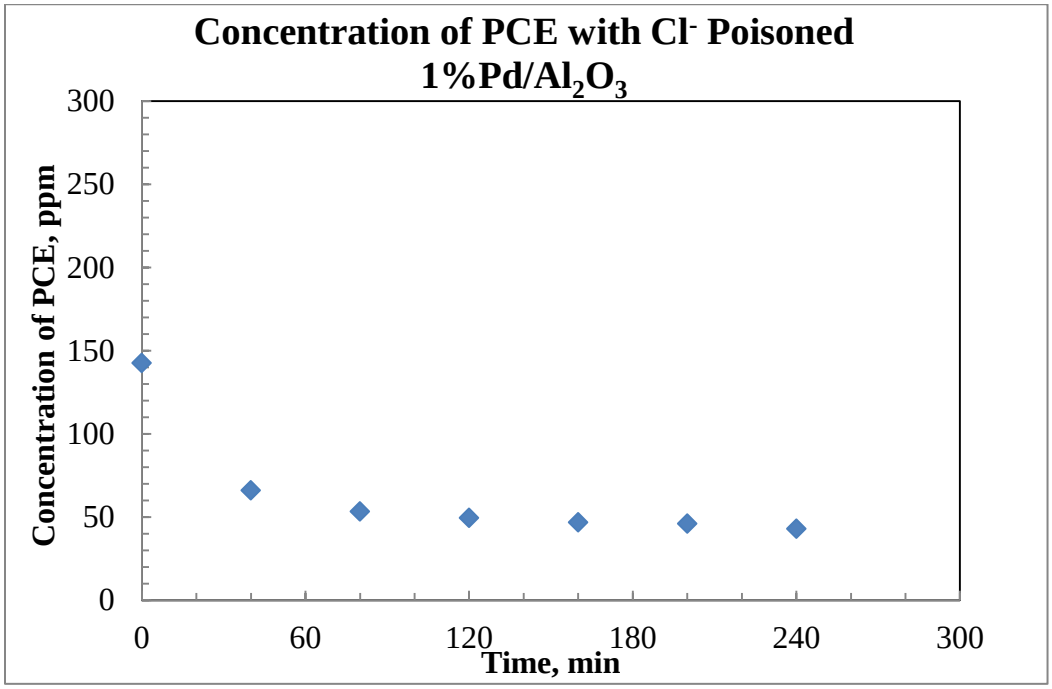

Figure 14: Concentration of PCE as a function of time with NaCl poisoned 1%Pd/Al_2O_3 catalyst [28]

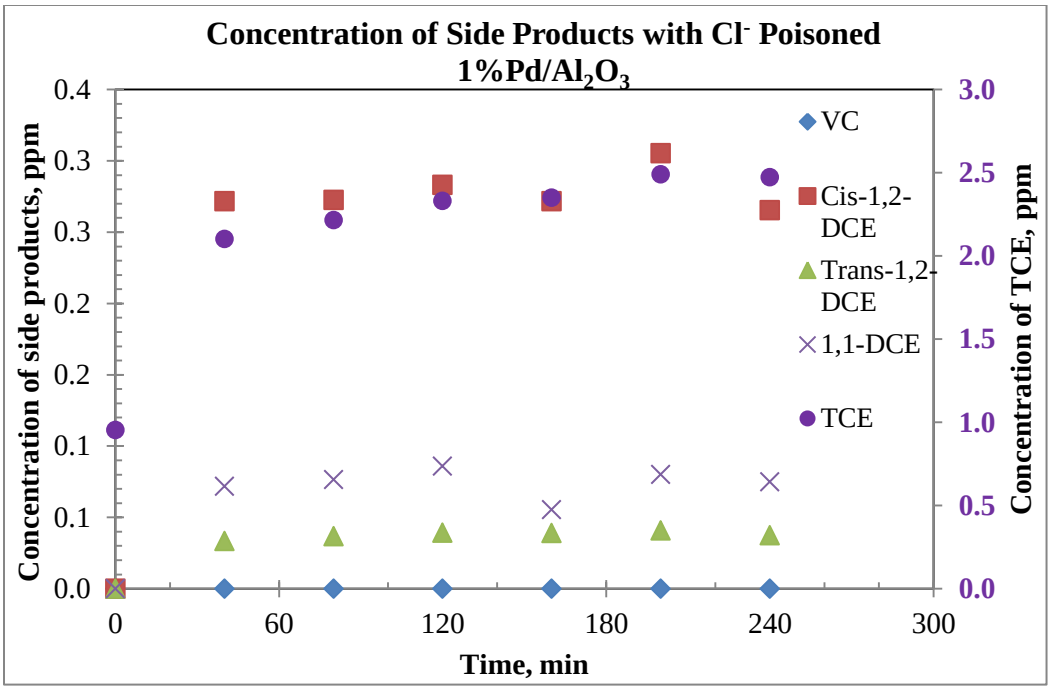

Figure 15: Concentration of side products as a function of time with NaCl poisoned 1%Pd/Al_2O_3 catalyst [28]

The concentrations of the products from the hydrodechlorination which used the 0.1M NaCl poisoned 1%Pd/SOMS catalyst are included on the next page in Figures 16 and 17. Figure 16 indicates that the use of the NaCl poisoned synthesized catalyst does indeed result in a higher concentration of PCE, with a final concentration of about 58 ppm, as compared to the final concentration of the fresh SOMS catalyst, which was approximately 33 ppm. Figure 17 reinforces this trend, as the concentrations of the byproducts remain high, just like the concentrations of the fresh SOMS catalyst. These trends are consistent with the results of the 0.1M NaCl poisoned Al_2O_3 supported catalyst.

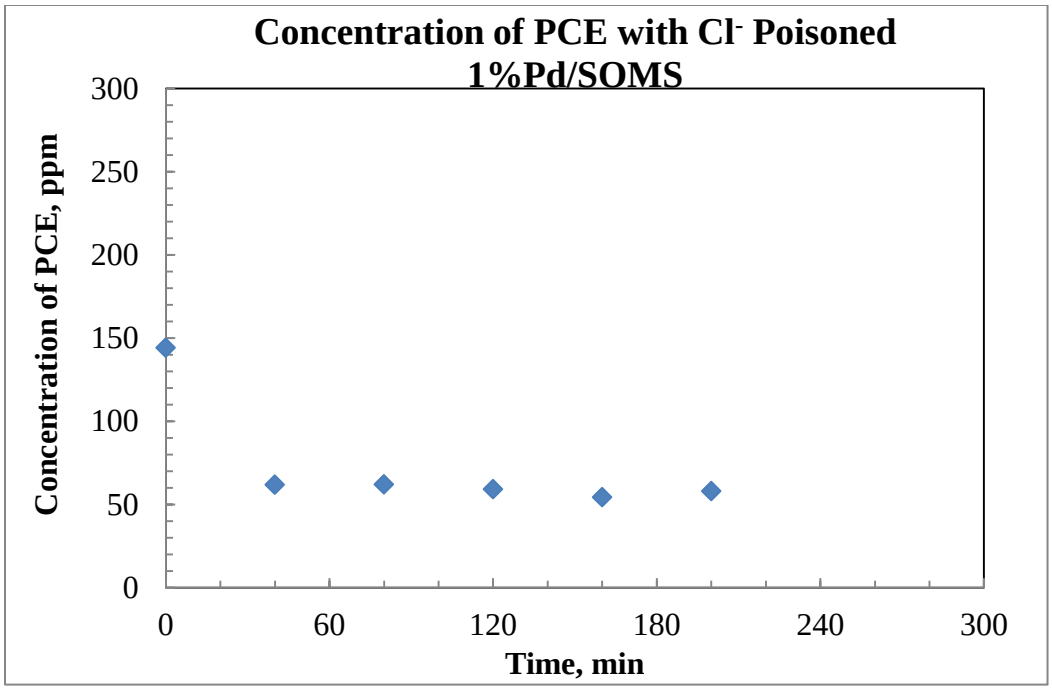

Figure 16: Concentration of PCE as a function of time for NaCl poisoned 1%Pd/SOMS catalyst [28]

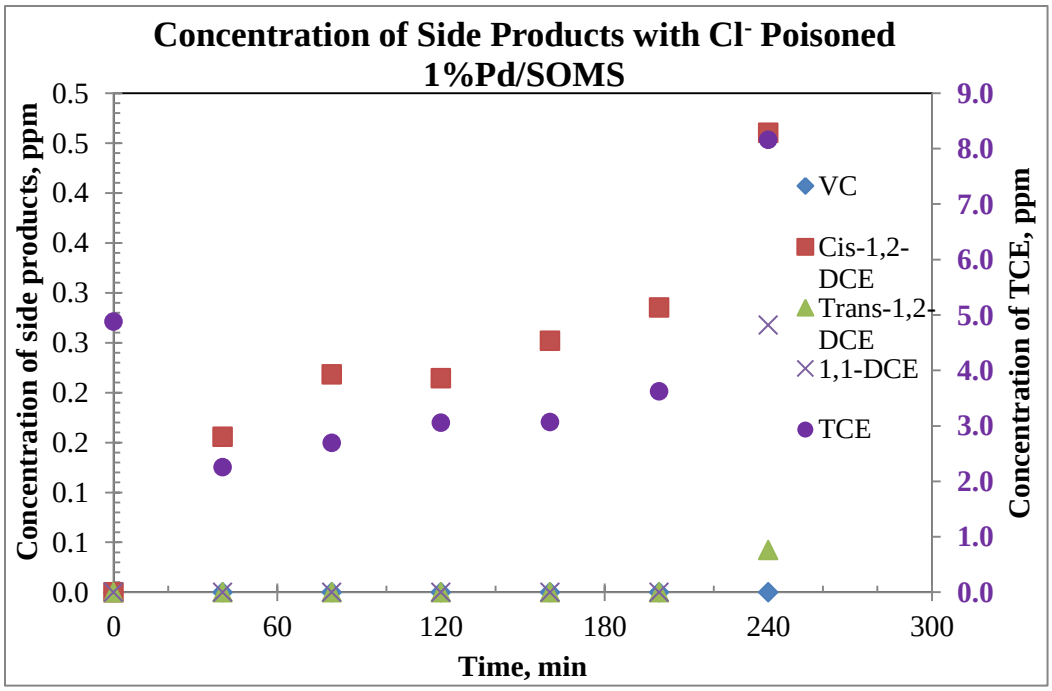

Figure 17: Concentration of byproducts achieved by NaCl poisoned 1%Pd/SOMS catalyst [28]

While the previous graphs indicate that the chlorine ion appears to have a poisoning effect on both the commercial and synthesized catalysts, this effect has not yet been quantified. The following graph, Figure 18, does this by comparing the PCE conversion achieved by the poisoned catalysts to the fresh catalysts.

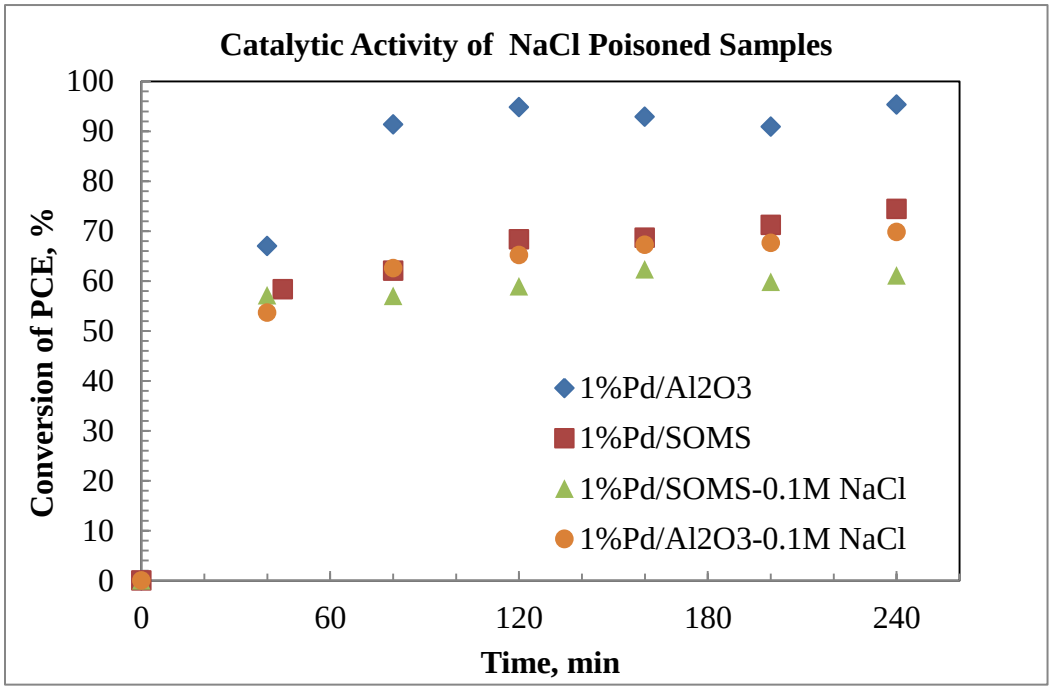

Figure 18: Poisoning effect of NaCl on commercial 1%Pd/Al2O3 and synthesized 1%Pd/SOMS catalysts [28]

Figure 18 indicates an important effect of the NaCl solution. As discussed earlier, the fresh commercial catalyst achieves 95% conversion of PCE. The Cl^- poisoned commercial catalyst, however, achieves only 70% conversion, which means the catalytic activity of the 1%Pd/Al_2O_3 catalyst drops approximately 25% when poisoned with the chlorine ion, which is an important groundwater species. The fresh synthesized catalyst achieves 75% PCE conversion, while the poisoned 1%Pd/SOMS catalyst still achieves 61% PCE conversion. This means that the reduction in the catalytic activity of the synthesized catalyst when poisoned by chlorine ions

is only about 14%. Since the reduction in catalytic performance of the synthesized catalyst (14%) is less than the reduction in performance experienced by the commercial catalyst (25%), and all other experimental conditions were kept the same, it can be concluded that the SOMS supported catalyst is less affected by the chlorine ion than the traditional Al_2O_3 supported catalyst.

4.2.4 Effect of Poisoning with NaHS

Lastly, the effect of poisoning the commercial and synthesized catalysts with 0.1M NaHS was examined. These results are especially significant, as the HS^- ion is the most frequently occurring ionic species in groundwater [29]. Figure 19 below demonstrates the concentration of PCE in the hydrodechlorination product samples over the span of four hours. These results suggest that hydrodechlorination has not been able to convert the PCE, as the concentrations stay relatively stable around 150 ppm for the entire reaction period of four hours.

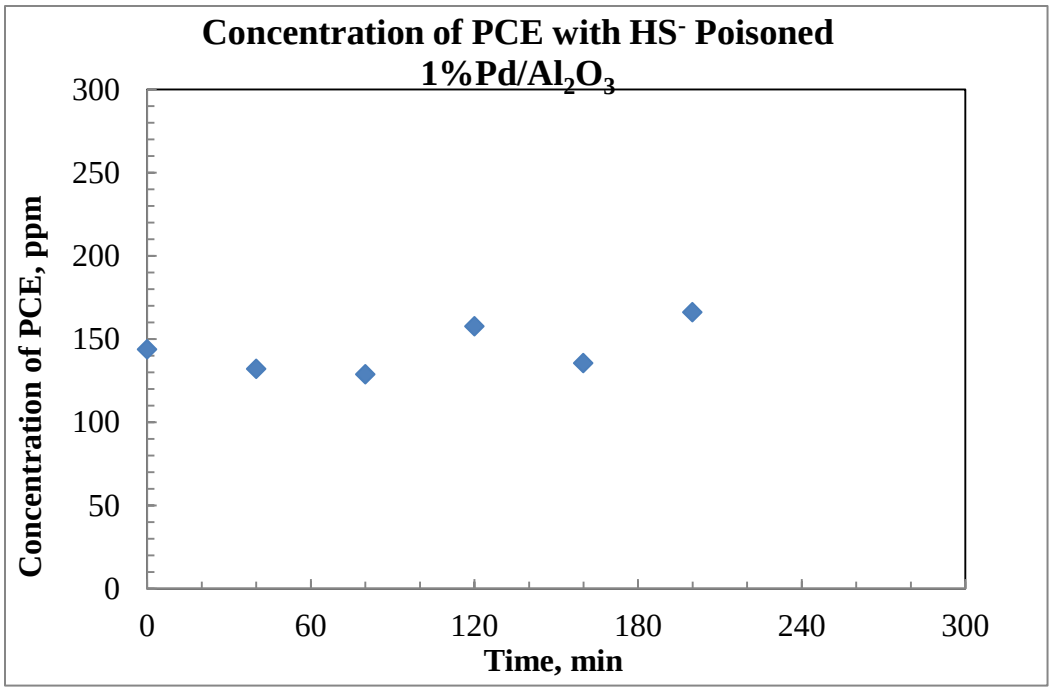

Figure 19: Concentration of PCE as a function of time with NaHS poisoned 1%Pd/Al_2O_3 catalyst [28]

This conclusion is corroborated by the distribution of side products' concentrations, as can be seen in Figure 20. Here the concentration of TCE remains steady at approximately 2.7 ppm, which indicates that hydrodechlorination is not occurring.

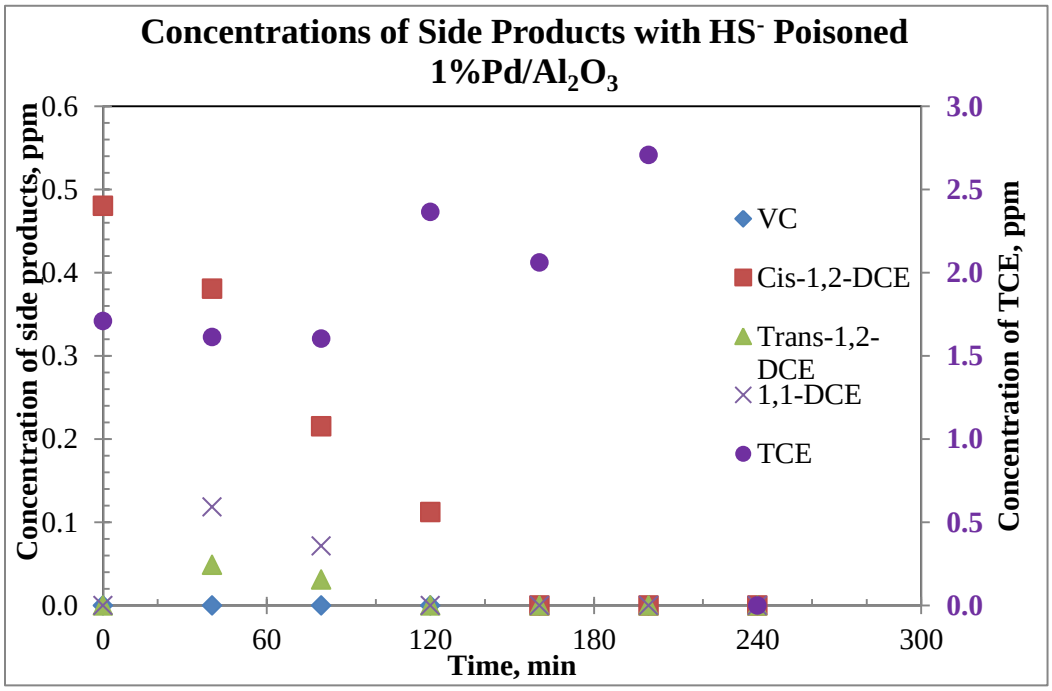

Figure 20: Concentration of side products as a function of time with NaHS poisoned 1%Pd/Al_2O_3 catalyst [28]

Figures 21 and 22 on the next page demonstrate the distribution of concentrations for the products of the hydrodechlorination reaction that used the HS^- poisoned synthesized catalyst. As was the case with Figure 16, which showed the concentration of PCE with the HS^- poisoned commercial catalyst, the concentration of PCE stays relatively high. The SOMS supported catalyst, however, does achieve a lower final concentration of approximately 135 ppm. Figure 22 below indicates the side product concentrations of the hydrodechlorination reaction with the HS^- poisoned SOMS catalyst. Similarly to the side products' concentrations of the HS^- Al_2O_3 supported catalyst, the TCE concentration of the SOMS supported catalyst stays approximately

the same over the span of four hours, however, the cis-1,2-dichloroethylene product concentration does reduce over time.

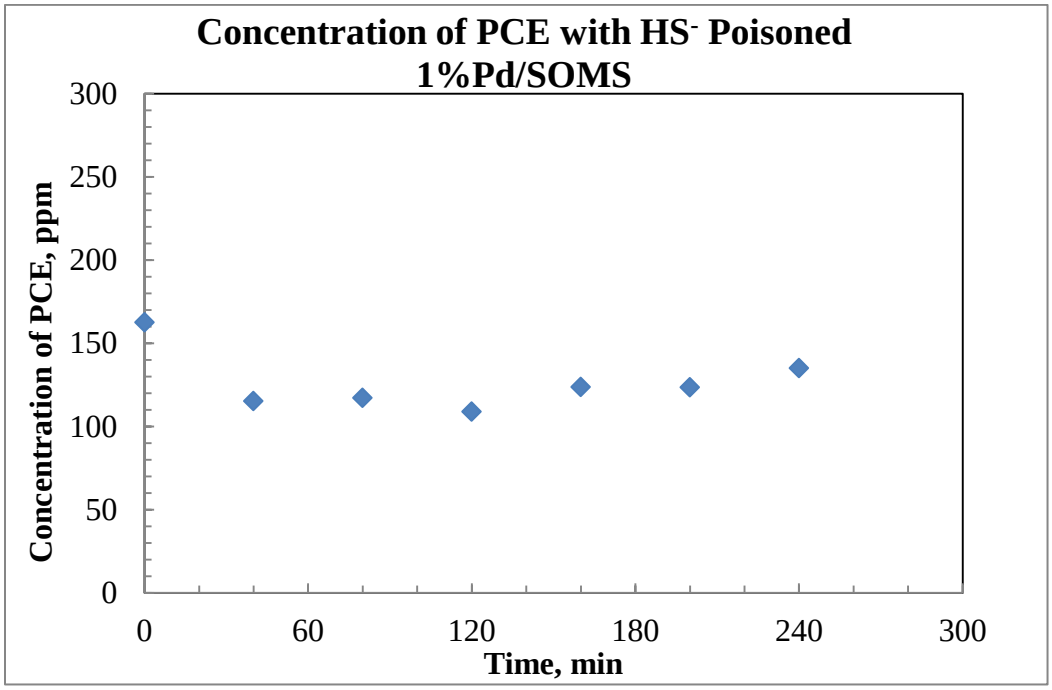

Figure 21: Concentration of PCE as a function of time with NaHS poisoned 1%Pd/SOMS catalyst [28]

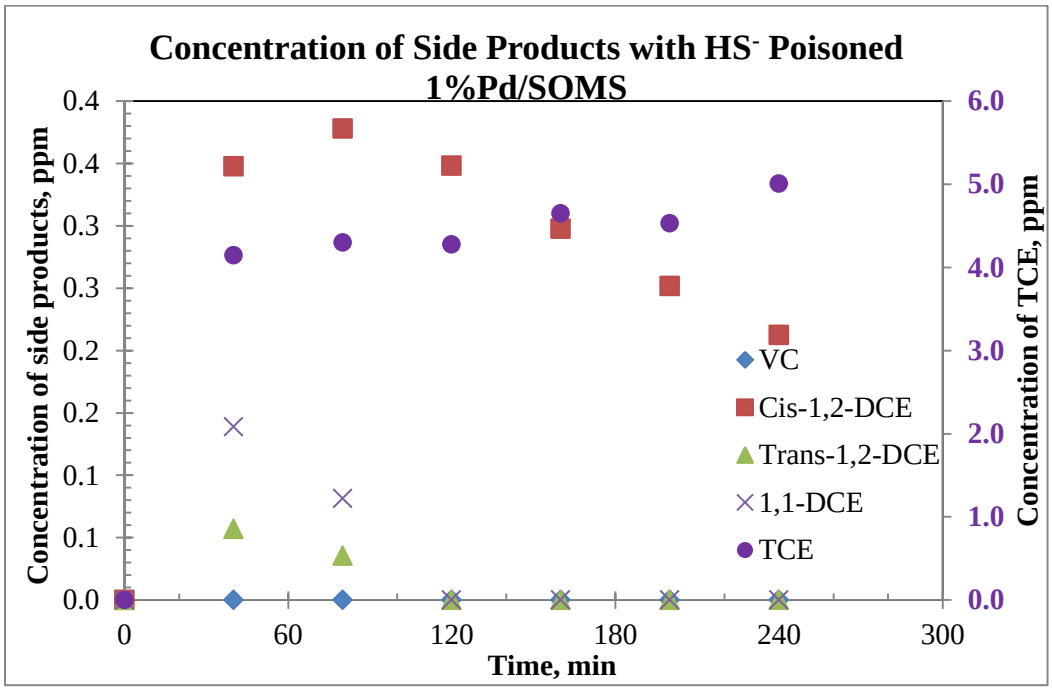

Figure 22: Concentration of side products as a function of time with NaHS poisoned 1%Pd/SOMS catalyst [28]

Simply reviewing concentration results can be misleading, as initial concentrations between different experiments may differ. In order to better understand the abilities of each catalyst tested, the conversion of PCE achieved by the HS^- poisoned catalysts will be compared.

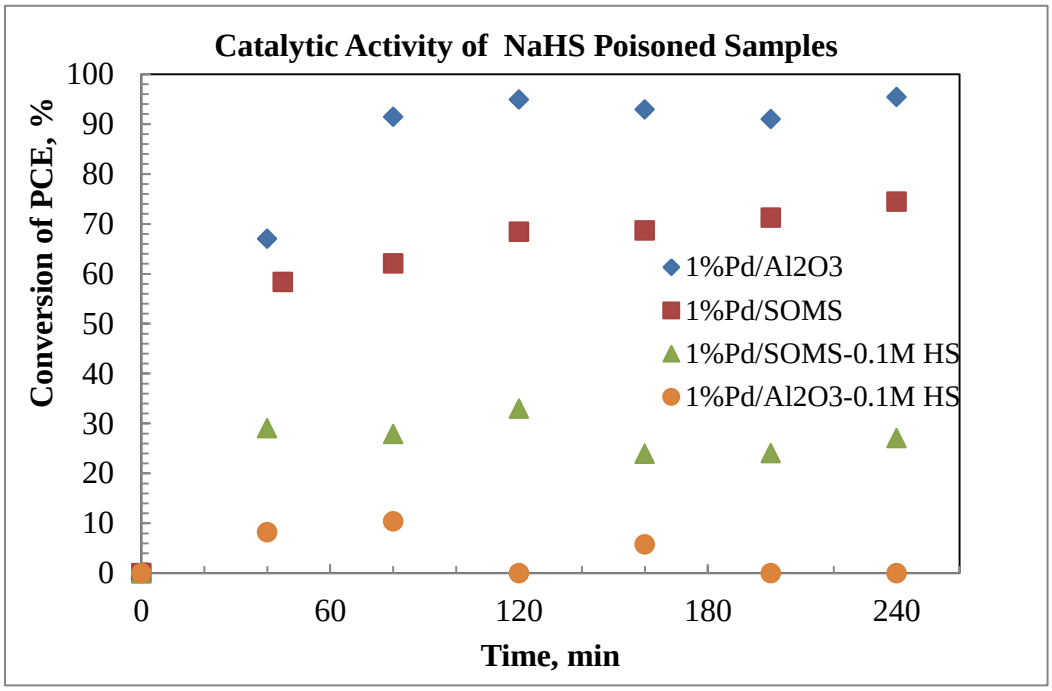

Figure 23: Poisoning effect of NaHS on commercial 1%Pd/Al2O3 and synthesized 1%Pd/SOMS catalysts [28]

Figure 23 above indicates particularly encouraging results, especially due to the significance of HS^- ions in groundwater. When the 1%Pd/Al_2O_3 catalyst is poisoned with 0.1M NaHS, the catalytic activity effectively drops to zero, as 0% conversion of PCE is achieved in four hours. Therefore, the Pd catalyst cannot perform hydrodechlorination when it is supported by Al_2O_3 and in the presence of HS^- ions. When the Pd catalyst is supported by the SOMS material, however, it can still achieve PCE conversion in the presence of HS^- ions. Based on Figure 25, the 1%Pd/SOMS catalyst achieves 27% conversion of PCE in four hours, whereas the 1%Pd/Al_2O_3 catalyst achieves 0% conversion. Since all experimental conditions were kept the

same between the two experiments, other than the type of support used, it can determined that the SOMS support better protects the catalyst from deactivating ionic species in order to achieve hydrodechlorination.

4.3 Characterization Studies Results and Discussion

Transmission IR data were collected on ex-situ poisoned samples of 1%Pd/Al_2O_3 with 0.1M NaCl, 0.1M Na_2SO_4, and 0.1M NaHS. The fresh commercial catalyst was used as a background, so that the effect of poisoning could be quantified. Figure 24 below indicates the IR spectra of the three poisoned samples. Each spectrum displays two v_{OH} bands at 3350cm^{-1} and 1650 cm^{-1}due to the absorbed water on the samples [30, 31]. The poisoned samples were dried at 110°C, however, not all of the water from the poisoning process could be dried, which is why these two peaks appear.

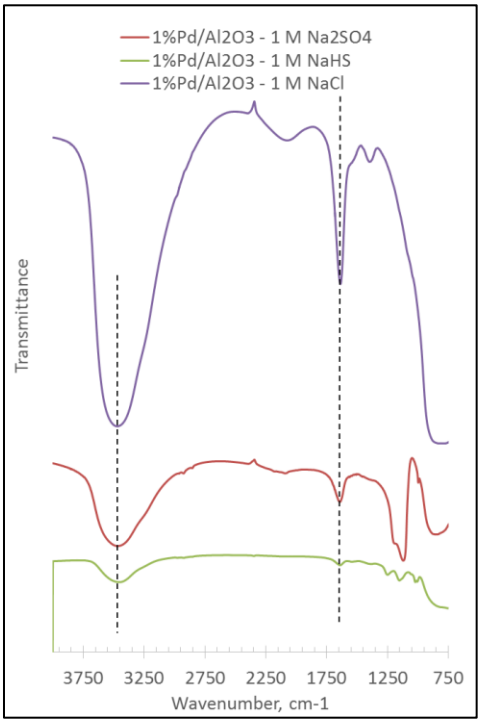

Figure 24: Full IR spectra for poisoned commercial catalysts. [32]

In order to better understand the effect of poisoning, the low wavenumber region was examined in closer detail- this is shown in Figure 25 below.

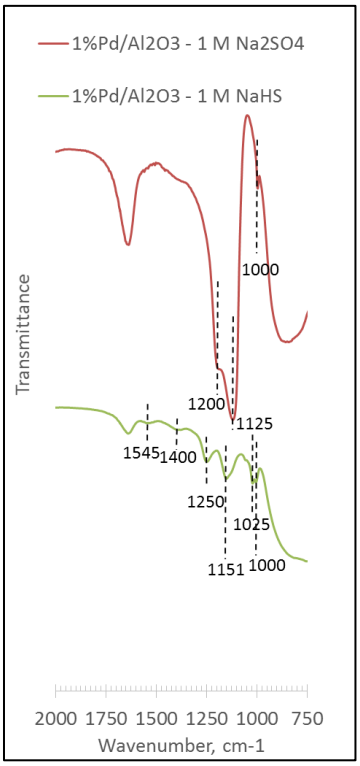

Figure 25: Low wavenumber region of IR spectra for poisoned commercial catalysts. [32]

The low wavenumber region includes the S=O stretching region from 1500 cm^{-1} to 1000 cm^{-1} [31]. There were no peaks associated with Pd-Cl or Al-Cl since these interactions are only viewable in the far-IR region (500cm^{-1} to 200 cm^{-1}). It is also possible that the Pd-Cl interactions are hidden due to the low metal loading of Pd. The SO_4^{2-} poisoned commercial catalyst exhibited three peaks at 1200 cm^{-1}, 1125 cm^{-1}, and 1000 cm^{-1}. The HS- poisoned commercial catalyst exhibited peaks at 1545 cm^{-1}, 1400 cm^{-1}, 1250 cm^{-1}, 1151 cm^{-1}, 1025 cm^{-1}, and 1000 cm^{-1}. As can be seen from the peak positions, the surface functional groups are not the same between the HS^- and SO_4^{2-} poisoned commercial catalysts. The common peak at 1000 cm^{-1} is

due to the sulfite species over Al_2O_3. For the hydrogen sulfide poisoned catalyst, the peak at 1400 cm^{-1} is most likely due to $Al_2(SO_4)_3$ and 1188 cm^{-1} could be due to the bulk absorbed $Al_2(SO_4)_3$. For the sulfate poisoned catalyst, the peak at 1200 cm^{-1} is also most likely due to an absorbed SO_2 species on the alumina surface. The peak at 1125 cm^{-1} most likely is due to the surface $Al_2(SO_4)_3$ [33]. As can be seen from the above spectra, the interactions with sulfur containing species greatly affect the surface functional groups of the catalysts.

Transmission spectra were also collected on the ex-situ poisoned 1%Pd/SOMS with 0.1M NaCl, 0.1M Na_2SO_4, and 0.1M NaHS. The fresh 1%Pd/SOMS catalyst was used as a background in order to better quantify the effect of poisoning more clearly. The transmission spectra for the three poisoned samples are included below in Figure 26.

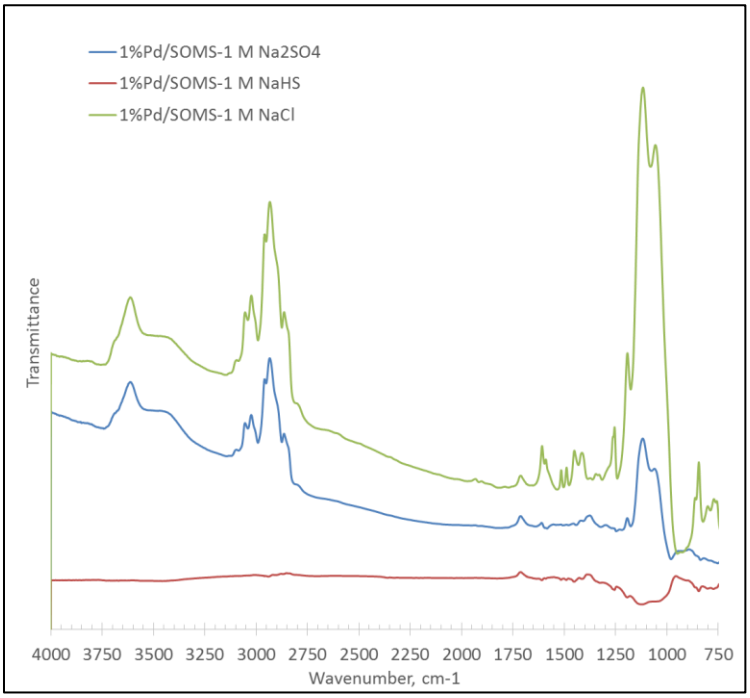

Figure 26: IR spectra for poisoned synthesized catalysts. [32]

A significant difference between the 1%Pd/SOMS and 1%Pd/Al_2O_3 spectra is the absence of the two v_{OH} peaks at 3350 cm^{-1} and 1650 cm^{-1} in the SOMS supported spectra. Although both materials were exposed to the same amount of water for the same duration, OH bands are not present in Figure 26. This is most likely due to the hydrophobic nature of the SOMS material, which would decrease the interaction between the water molecules and the SOMS support. As SOMS materials are organo-silica compounds, both carbon and silica groups are present in the structure. The bands in Figure 26 between 3250 cm^{-1} and 2750 cm^{-1} might be due to these interactions on the C-H bonds with the poisoning solutions [34]. In the low wavenumber region, there are also several peaks that may be significant. At this time, these peaks could not be identified or attributed to particular compounds, due to the complex nature of the structure of SOMS as well as the lack of literature on sulfur poisoning of organo-silica materials. It was determined that the results of the transmission IR measurements will be considered in conjunction with the results of other surface spectroscopy techniques in future work.

5. Conclusion and Recommendations

In this research project, the hydrodechlorination activity associated with two different support materials, Al_2O_3 and SOMS, was compared both with and without the presence of potentially deactivating ionic species. The hydrodechlorination experiments reported in this paper indicate that when poisoning is not considered, the performance of the commercial, 1%Pd/ Al_2O_3 catalyst was significantly better than the performance of the synthesized 1%Pd/SOMS catalyst- the commercial catalyst achieved 95% conversion of PCE, while the synthesized catalyst achieved only 70% conversion. When the catalysts encountered the chlorine or hydrogen sulfide ion, however, performance of the Al_2O_3 supported catalyst was drastically reduced, while the SOMS catalyst was not as significantly impacted. It was determined that the sulfate ion was did not have a poisoning effect on the Pd catalyst, and does not need to be considered further. Based on these encouraging results, it can be concluded that using SOMS as a catalytic support considerably improves the hydrodechlorination activity of the Pd catalysts.

Characterization studies were conducted to determine the changes to surface functional groups of the catalytic support materials due to poisoning. It was determined that interactions with sulfur containing species greatly affect the surface functional groups of the catalysts, and that the SOMS supported catalyst better repels water, due to the absence of the two OH bands that were seen for the Al_2O_3 supported catalyst. Lastly, it was determined that the SOMS IR spectra low wavenumber region should be investigated further in conjunction with other characterization studies due to its complexity.

It is recommended that future research be conducted to increase the activity of the fresh SOMS supported catalyst. This could be done by changing synthesis and reduction parameters, such as Pd content, solvent used in experiment, length of experiment. Another area of future

work could be testing different conditions of HS^- poisoning, in order to better understand the limitations of the SOMS support. Additionally, further characterization studies could be undertaken in order to better understand the nature of the synthesized catalyst-support combinations. Characterization studies could also help pinpoint the exact reason why SOMS better acts as a support than the traditional Al_2O_3. Lastly, further experiments that run the reactions at different temperatures could be conducted, in order to determine k as a function of temperature. This could help lead to a better understanding of the kinetics of the commercial and synthesized catalysts when used in hydrodechlorination.

6. References

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APPENDIX A:

Raw Data

Table A1: HPLC Data obtained for Fresh 1%Pd/Al_2O_3 Catalyst

Time	Retention Time	Area	Height	Conc, ppm	Conc, ppm Corrected	Conc μM Corrected
THF						
0	9.159	122984	9797	433.3	450.0	6240.8
40	9.098	126084	9978	444.2	450.0	6240.8
80	9.078	135074	10034	475.8	450.0	6240.8
120	9.132	136206	9997	479.8	450.0	6240.8
160	9.084	128623	9949	453.1	450.0	6240.8
200	9.129	130732	9834	460.5	450.0	6240.8
240	9.077	136961	10136	482.5	450.0	6240.8
TCE						
0	23.18	646504	37985	8.6	8.9	67.8
40	23.055	409992	24156	5.4	5.5	41.9
80	23.087	263804	15297	3.5	3.3	25.2
120	23.109	201580	11851	2.7	2.5	19.1
160	23.043	158476	9517	2.1	2.1	15.9
200	23.055	148488	8844	2.0	1.9	14.6
240	23.012	123458	7187	1.6	1.5	11.6
PCE						
0	28.689	15306641	845852	277.3	288.0	1736.8
40	28.596	5177945	286517.0	93.8	95.0	573.1
80	28.645	1447785	81038	26.2	24.8	149.6
120	28.653	869734	49283	15.8	14.8	89.1
160	28.586	3033794	170099	55.0	54.6	329.1
200	028.569	1472955	83484	26.7	26.1	157.2
240	28.553	786774	43853	14.3	13.3	80.2
Cis-1,2-dichloroethylene						
0	17.278	38143	2409	0.5	0.5	5.0
40	17.134	30911	1862	0.4	0.4	3.9
80	17.145	16987	1046	0.2	0.2	2.0
120	17.223	9135	570	0.1	0.1	1.1
160	0	0	0	0.0	0.0	0.0
200	0	0	0	0.0	0.0	0.0
240	0	0	0	0.0	0.0	0.0
Trans-1,2-dichloroethylene						
0	18.995	12351	770	0.1	0.1	0.6
40	18.856	10843	682	0. 0	0.0	0.5
80	18.877	6740	386	0.0	0.0	0.3
120	0	0	0	0.0	0.0	0.0

160	0	0	0	0.0	0.0	0.0
200	0	0	0	0.0	0.0	0.0
240	0	0	0	0.0	0.0	0.0
1,1-Dichloroethylene						
0	20.45	14813	870	0.2	0.2	2.0
40	20.315	9323	569	0.1	0.1	1.2
80	20.306	5452	365	0.1	0.1	0.7
120	0	0	0	0.0	0.0	0.0
160	0	0	0	0.0	0.0	0.0
200	0	0	0	0.0	0.0	0.0
240	0	0	0	0.0	0.0	0.0

Table A2: HPLC Data obtained for Fresh 1%Pd/SOMS Catalyst

Time	Retention Time	Area	Height	Conc, ppm	Conc, ppm Corrected	Conc μM Corrected
THF						
0	9.151	107379	8755	378.3	450.0	6240.8
40	9.147	112704	8740	397.0	450.0	6240.8
80	8.963	107586	8653	379.0	450.0	6240.8
120	9.095	117884	8766	415.3	450.0	6240.8
160	9.109	115434	8716	406.7	450.0	6240.8
200	9.095	114687	8741	404.0	450.0	6240.8
240	9.092	115324	8788	406.3	450.0	6240.8
TCE						
0	23.07	715147	40930	9.5	11.3	85.9
40	23.027	338394	20067	4.5	5.1	38.7
80	22.832	343486	19876	4.6	5.4	41.2
120	22.988	340027	19836	4.5	4.9	37.2
160	22.991	360235	20823	4.8	5.3	40.2
200	23.03	340810	19947	4.5	5.0	38.3
240	23.013	323828	18961	4.3	4.8	36.2
PCE						
0	28.642	6043764	325402	109.5	130.2	785.4
40	28.58	2643408	145165	47.9	54.3	327.3
80	28.444	2297617	125388	41.6	49.4	298.0
120	28.546	2098368	116371	38.0	41.2	248.4
160	28.542	2036310	112733	36.9	40.8	246.2
200	28.546	1856048	102945	33.6	37.4	225.8

240	28.541	1658724	91578	30.0	33.3	200.7
Cis-1,2-Dichloroethylene						
0	17.175	17351	1083	0.2	0.3	2.6
40	17.156	33447	2089	0.4	0.5	4.8
80	16.855	38821	2306	0.5	0.6	5.8
120	17.094	43127	2605	0.5	0.6	5.9
160	17.1	45616	2811	0.6	0.6	6.3
200	17.094	44985	2804	0.5	0.6	6.3
240	17.102	45826	2793	0.6	0.6	6.4
Trans-1,2-Dichloroethylene						
0	19.175	4183	0	0.0	0.0	0.2
40	18.884	6803	380	0.0	0.0	0.4
80	18.614	6940	422	0.0	0.0	0.4
120	18.807	9254	534	0.0	0.0	0.5
160	18.814	9878	573	0.0	0.0	0.5
200	18.794	10009	569	0.0	0.0	0.5
240	18.83	8225	508	0.0	0.0	0.4
1,1-Dichloroethylene						
0	20.353	7017	381.0	0.1	0.1	1.1
40	20.31	9216	533	0.1	0.1	1.3
80	20.082	9139	552	0.1	0.1	1.4
120	20.271	9788	599	0.1	0.1	1.4
160	20.272	11360	688	0.1	0.2	1.6
200	20.291	11334	669	0.1	0.2	1.6
240	20.287	10816	654	0.1	0.2	1.5

APPENDIX B:

Sample Calculations

PCE Calibration Factor:

$$\beta_{PCE} = \frac{C_{PCE} \times V_{loop}}{A_{PCE}}$$

$$\beta_{PCE} = \frac{1000\ ppm}{53120464} = 0.00001812\ ppm/area$$

PCE Concentration:

$$C_{PCE} = C_{THF} \times \left(\frac{\beta_{PCE}}{\beta_{THF}}\right) \times \left(\frac{A_{PCE}}{A_{THF}}\right)$$

$$C_{PCE} = (450ppm) \times \left(\frac{0.00001812}{0.00352285}\right) \times \left(\frac{170099}{128623}\right) = \mathbf{54.6\ ppm}$$

PCE Conversion:

$$X_{PCE} = \frac{C_{PCE,0} - C_{PCE,t}}{C_{PCE,0}}$$

$$X_{PCE} = \frac{288\ ppm - 54.6\ ppm}{288\ ppm} = \mathbf{0.8104}$$